

# (12) UK Patent Application (19) GB (11) 2 291 653 (13) A

(43) Date of A Publication 31.01.1996

(21) Application No 9514800.3

(22) Date of Filing 19.07.1995

(30) Priority Data

(31) 9414957

(32) 25.07.1994

(33) GB

(71) Applicant(s)

Glaverbel

(Incorporated in Belgium)

Chaussee De La Hulpe 166, B-1170 Brussels, Belgium

(72) Inventor(s)

Philippe Legrand

Robert Terneu

Karel Vandiest

Michel Hannotiau

(74) Agent and/or Address for Service

Hyde, Heide & O'Donnell

10-12 Priests Bridge, LONDON, SW15 5JE,

United Kingdom

(51) INT CL<sup>6</sup>

C03C 17/34 , C23C 16/30 18/12

(52) UK CL (Edition O )

C7F FQ913 FQ914 FQ916 FR903 FR908 FR913 FR914

F782

U1S S1714 S3037 S3077

(56) Documents Cited

GB 2262749 A EP 0650938 A1 EP 0548972 A1

EP 0530876 A2 WO 90/09883 A1 US 5183700 A

WPI Accession No. 91-040588/06 & JP 2307843 A WPI

Accession No. 88-261449/37 & JP 63190742 A

(58) Field of Search

UK CL (Edition N ) C7F FHB FHE FHX

INT CL<sup>6</sup> C03C 17/34 , C23C 14/06 14/08 16/30 16/34

16/40 18/12 28/04

ONLINE:WPI,CLAIMS

(54) A pyrolytically coated glazing panel

(57) A pyrolytically coated glazing panel, in which the reflected colour remains substantially constant as changes in the relative thicknesses of the coating layers are made in order to optimise optical properties, comprises a vitreous material substrate, an undercoat layer comprising a nitride selected from nitrides of titanium, zirconium, niobium and mixtures of two or more thereof and an exposed transparent overcoat layer adjacent said undercoat layer comprising an oxide. The panel is characterised in that the total geometrical thickness of the undercoat and overcoat layers is between 20 nm and 55 nm. The oxide of the overcoat layer is selected from oxides of aluminium, silicon, magnesium, tin, zinc, zirconium, titanium, bismuth, niobium and mixtures thereof. A further coating layer may be positioned between the undercoat layer and the substrate. This may be silicon oxide and have a thickness of 5 - 10 nm.

GB 2 291 653 A

### A pyrolytically coated glazing panel

This invention relates to transparent solar control glazing panels. In particular, the invention relates to a pyrolytically coated glazing panel comprising a substrate, an undercoat layer comprising a nitride and an exposed transparent overcoat layer adjacent said undercoat layer comprising a metal oxide.

Pyrolysis generally has the advantage of producing a hard coating, which precludes the need for a protective layer. The coatings formed by pyrolysis have durable abrasive- and corrosion-resistant properties. It is believed that this is due in particular to the fact the process involves depositing of coating material onto a substrate which is hot. Pyrolysis is also generally cheaper than alternative coating processes such as sputtering, particularly in terms of the investment in plant. The deposit of coatings by other processes, for example by sputtering, lead to products with very different properties, in particular a lower resistance to abrasion and occasionally a different refractive index.

Reflective transparent solar control glazing panels have become a useful material for architects to use for the exterior facade of buildings. Such panels have aesthetic qualities in reflecting the immediate environment and, being available in a number of colours, in providing a design opportunity. Such panels also have technical advantages by providing the occupants of a building with protection against solar radiation by reflection and/or absorption and eliminating the dazzling effects of intense sunshine, giving an effective screen against glare, enhancing visual comfort and reducing eye fatigue. There exist a number of documents which describe glazing panels having a coating providing protection against solar radiation. Thus in EP-A-239280 (Gordon) there are described transparent glass sheets comprising thereon titanium nitride of at least 30 nm thickness as the principal solar screening layer for reducing transmission in the near infrared and thereover a layer of tin oxide of about 30 to 80 nm thickness. The tin oxide serves to protect the titanium nitride from oxidation and increases abrasion resistance.

It is known that, by changing the relative thicknesses of coating layers, changes in optical properties will result. Thus, in order to optimise optical properties, it is desirable to make use of particular relative thicknesses of the

coating layers. However, it is generally expected that, for a given selection of coating materials, changes in coating thickness result in changes the dominant wavelength (i.e. colour) of reflected light. For example, in a solar control glazing panel comprising a first coating of titanium nitride and a layer of iron, cobalt and chromium oxides, a variation in the colour of reflected light is found when the thickness of the oxide layer is changed. Thus, measurement of the properties of samples of such panels carrying coatings formed by chemical vapour deposition on 4 mm glass were found to be as set out in the following Table I.

TABLE I

SAMPLE:	A	B
Nitride	TiN	TiN
Thickness (nm)	45	45
Oxide	s	s
Thickness	32.5	45
T <sub>L</sub> (%)	14	12
<sup>1</sup> FS (%)	26	26
<sup>1</sup> R <sub>L</sub> (%)	28	24
<sup>1</sup> T <sub>L</sub> /FS	0.53	0.45
Reflected colours from coated side	grey	blue
Purity (%)	5	15

<sup>1</sup> = as measured from the un-coated side.

s = Mixture of iron, cobalt and chromium oxides in the weight proportions of 26:61:13.

It is an object of the present invention to provide pyrolytically coated glazing panels in which the reflected colour remains substantially constant as changes in the relative thicknesses of the coating layers are made in order to optimise optical properties.

We have now surprisingly discovered that this object can be achieved, for specific coating materials applied at a specific total coating thickness.

According to a first aspect of the invention there is provided a pyrolytically coated glazing panel comprising a substrate, an undercoat layer comprising a nitride selected from nitrides of titanium, zirconium, niobium and mixtures of two or more thereof and an exposed transparent overcoat layer adjacent said undercoat layer comprising an oxide, characterised in that the total geometrical thickness of the undercoat and overcoat layers is between 20 nm and 55 nm.

The substrate is preferably in the form of a ribbon of vitreous material, such as glass or some other transparent rigid material. In view of the proportion of incident solar radiation which is absorbed by the glazing panel, especially in environments where the panel is exposed to strong or long-term solar radiation, there is a heating effect on the glass panel which may require that the glass substrate be subsequently subjected to a toughening process. However, the durability of the coating enables the glazing panel to be mounted with the coated face outermost, thus reducing the heating effect.

Preferably, the substrate is clear glass, although the invention also extends to the use of coloured glass as the substrate.

Preferably the geometrical thickness of the undercoat layer is between 10 nm and 50 nm. This thickness range is particularly suitable for industrial manufacture, and allows an effective anti-solar effect to be obtained while maintaining a sufficient level of luminous transmission of the panel.

Preferably the geometrical thickness of the overcoat layer is between 9 nm and 35 nm, preferably from 15 to 35 nm. The refractive index of the overcoat layer is preferably from 1.8 to 2.7. The material of the transparent overcoat layer includes materials which have a "refractive index"  $n(\lambda)$  which is greater than, preferably substantially greater than the value of the "spectral absorption index"  $k(\lambda)$  over the whole of the visible spectrum (380 to 780 nm). Definitions of refractive index and spectral absorption index can be found in International Lighting Vocabulary, published by the International Commission on Illumination (CIE), 1987, pages 127, 138 and 139. In particular, we have found advantage in choosing a material for which the refractive index  $n(\lambda)$  is greater than 10 times the spectral absorption index  $k(\lambda)$  over the wavelength range 380 to 780 nm. The overcoat layer is preferably an oxide layer. The transparent material of the overcoat layer may be independently selected from oxides of aluminium, bismuth, magnesium, niobium, silicon (both  $\text{SiO}_x$  and  $\text{SiO}_2$ ), tin, titanium (both rutile and anatase), zinc and mixtures of two or more thereof. The following table lists the refractive index  $n(\lambda)$  and the spectral absorption index  $k(\lambda)$  of a number of suitable transparent materials over the range 380 nm to 780 nm.

TABLE II

Material	n( $\lambda$ )	k( $\lambda$ )
MgO	1.77 - 1.73	0*
TiO <sub>2</sub> <sup>r</sup>	2.9 - 2.3	0*
Bi <sub>2</sub> O <sub>3</sub>	2.92 - 2.48	0.1 - 0*
TiO <sub>2</sub> <sup>a</sup>	2.64 - 2.31	0*
ZnO	2.3 - 2.02	0.08 - 0.001
SnO <sub>2</sub>	1.94 - 1.85	0*
Al <sub>2</sub> O <sub>3</sub>	1.79 - 1.76	0*
SiO <sub>2</sub>	1.47 - 1.45	0*
ZrO <sub>2</sub>	2.1	0*
SiO <sub>x</sub>	1.7	0*

Note:

r = rutile form

a = anatase form

0\* means less than 10<sup>-3</sup>

It is particularly preferred that the material of the transparent coating layer is titanium oxide and/or stannic oxide. The transparent coating layer is an outer layer, and for this reason stannic oxide is beneficial if a higher resistance to abrasion is required, such as where the panel is positioned with the coated face outermost.

In preferred embodiments of the invention, the nitride of the undercoat layer comprises titanium nitride and the oxide of the overcoat layer comprises tin oxide.

It should be noted that, in the oxide or nitride material layers, it is not essential for the metal and the oxygen or nitrogen to be present in stoichiometric proportions.

From a technical point of view, it is desired that the glazing panel shall not pass too great a proportion of total incident solar radiation in order that the interior of the building shall not become overheated in sunny weather. The transmission of total incident solar radiation may be expressed in terms of the "solar factor". As used herein, the term "solar factor" means the sum of the total energy directly transmitted and the energy which is absorbed and re-radiated on the side away from the energy source, as a proportion of the total radiant energy incident of the coated glass. The glazing panels according to the invention have a solar factor (FS) of less than 70%, preferably less than 60%.

It is also desired that the glazing panel shall also transmit a reasonable proportion of visible light in order to allow natural illumination of the interior of the building and in order to allow its occupants to see out. The transmission of visible light may be expressed in terms of the "transmission factor" as a proportion of the incident light falling on the coated substrate. Thus it is desirable to increase the selectivity of the coating, that is to increase the ratio of the transmission factor to the solar factor. Preferably, the light transmission factor ( $T_L$ ) of the panel according to the invention is between 30% and 65%.

Preferably, the panel has a mean ultra violet transmission ( $T_{UV}$ ), over the ultra violet spectrum (280 nm to 380 nm), of less than or equal to 45%, most preferably less than or equal to 20%, which can be beneficial in reducing damage to light sensitive materials inside the building.

We prefer that the composition and thickness of the undercoat and overcoat layers are such that the dominant wavelength reflected from the un-coated side of the panel in the visible region lies within the range of 470 to 490 nm (blue). From an aesthetic point of view, it is preferred to provide glazing panels with a blue colour in reflection. Where buildings have a relatively large glazed area and also where high buildings are concerned, a blue reflected colour provides a less obtrusive appearance to the observer. In other embodiments, glazing panels with a neutral aspect are formed.

The reflectivity of visible light ( $R_L$ ) from the un-coated side is preferably from 10% to 30%. Preferably the purity of colour reflected from said un-coated side is greater than 5%, preferably at least 8% most preferably at least 15%, such as between 19% and 22%. The purity of a colour is defined according to a linear scale where a defined white light source has a purity of zero and the pure colour has a purity of 100%. By the term "colour purity" as used herein, we mean excitation purity measured with illuminant C as defined in International Lighting Vocabulary, published by the International Commission on Illumination (CIE), 1987, pages 87 and 89.

The overcoat layer may be selected to provide enhancement of the purity of colour reflected from the un-coated side of the panel, in comparison with a similar panel which is not provided with the oxide overcoat. Thus, for example, a glazing panel provided with a 40 nm thick coating of titanium nitride has a grey-blue colour (purity = 5%) in reflection from the un-coated side, whereas when an overcoat of 10 nm thick tin oxide is applied thereon the panel takes on a blue appearance from the un-coated side and the purity of colour rises to 8%. In the case of a 20 nm thick TiN coating, an overcoat of 20 nm  $\text{SnO}_2$  increases the purity of colour from 15% to 21%.

In one embodiment of the invention, no other coating layers will be present. Thus, the first layer is coated directly on the substrate. However, in an alternative embodiment of the invention the panel may further comprise a further coating layer positioned between said undercoat layer and said substrate. In particular, in order to reduce interaction between the reagents and the substrate during formation of the nitride layer, a coating layer of silicon oxide may be applied, as described in British patent specifications GB 2234264 and GB 2247691 (Glaverbel). The geometrical thickness of said further layer may be between 50 and 100 nm.

According to a second aspect of the invention, there is provided a process for forming a coated glazing panel comprising the steps of:

(i) forming an undercoat layer over a substrate by pyrolysis, said undercoat layer comprising a nitride selected from nitrides of titanium, zirconium, niobium and mixtures of two or more thereof; and

(ii) forming an exposed transparent overcoat layer adjacent said undercoat layer by pyrolysis, said overcoat layer comprising an oxide;

characterised in that the coating of said undercoat and overcoat layers is such that the total geometrical thickness thereof is between 20 nm and 55 nm.

The panels according to the invention may be installed in single or multi-glazed assemblies. The coated surface of the panel may be the inside surface of the exterior glazing panel. In this way the coated surface is not exposed to the ambient weather conditions which might otherwise more rapidly reduce its life by soiling, physical damage and/or oxidation. Coatings produced by pyrolysis generally have a greater mechanical resistance than coatings produced by other methods and they may be exposed to the atmosphere. The panels according to the invention may usefully be employed in laminated glass structures, for example where the coated surface is the inside surface of the exterior laminate.

The glazing panels according to the invention may be manufactured as follows. Each pyrolytic coating step may be carried out at a temperature of from 550°C to 750°C.

The coatings can be formed on a sheet of glass which moves in a tunnel oven or on a glass ribbon during formation, whilst it is still hot. The coatings can be formed inside the Lehr which follows the glass ribbon forming device or inside the float tank on the top face of the glass ribbon whilst the latter is floating on a bath of molten tin.

The coating layers are preferably applied to the substrate by chemical vapour deposition. Chemical vapour deposition is particularly preferred because it tends to lead to coatings of regular thickness and composition, uniformity of the product being particularly important where the glazing panels  
5 are to be used over large areas. With the use of liquids as the reactant materials, one cannot act over the vaporisation process. Furthermore, chemical vapour deposition is more economic in terms of raw materials, leading to lower wastage.

To form each coating, the substrate is brought into contact, in a coating chamber, with a gaseous medium comprising one or more substances in  
10 the gaseous phase. The coating chamber is fed with a reagent gas through one or more nozzles, the length of which is at least equal to the width to be coated. Depending on the type of coating to be formed and the reactivity of the substances used, if several substances have to be used, these are distributed either in the form of a mixture by a single ejection nozzle in the coating chamber,  
15 or separately by several ejection nozzles.

Methods and devices for forming such a coating are described for example in French patent No 2 348 166 (BFG Glassgroup) or in French patent application No 2 648 453 A1 (Glaverbel). These methods and devices lead to the formation of particularly strong coatings with advantageous optical  
20 properties.

To form coatings of tin oxide  $\text{SnO}_2$  or titanium dioxide  $\text{TiO}_2$ , two successive nozzles are used. The reagent carrying the metal (Sn or Ti), fed in at the first nozzle, is a tetrachloride, liquid at ambient temperature, vaporised in a current of anhydrous carrier gas at an elevated temperature. Vaporisation is  
25 facilitated by the atomisation of these reagents in the carrier gas. To produce the oxide, the molecules of tetrachloride are brought into the presence of water vapour conducted to the second nozzle. The water vapour is superheated and is also injected into a carrier gas.  $\text{SnO}_2$  may be formed for example using the proportions of  $\text{SnCl}_4$  and  $\text{H}_2\text{O}$  given in British patent specification GB 2026454  
30 (Glaverbel).

If desired, a dopant such as HF is added to the water vapour in order to form a conductive tin oxide coating.

Coatings of silicon oxide  $\text{SiO}_2$  or  $\text{SiO}_x$  may be deposited from silane  $\text{SiH}_4$  and oxygen in accordance with the descriptions in British patent  
35 specifications GB 2234264 and GB 2247691, referred to above.

The invention will now be described in more detail, with reference to the following non-limiting examples.



EXAMPLE 1

A substrate consisting of a 4 mm thick sheet of clear soda-lime glass was coated by pyrolysis in the following manner. An apparatus comprising two successive nozzles is used. A reagent comprising  $\text{TiCl}_4$ , vaporised in a current of anhydrous nitrogen gas at about  $600^\circ\text{C}$ , is fed in at the first nozzle. Vaporisation is facilitated by the atomisation of these reagents in the carrier gas. Ammonia gas is conducted to the second nozzle. The ammonia is heated to about  $600^\circ\text{C}$ , and is also injected into a carrier gas, which is air heated to about  $600^\circ\text{C}$ . The flow rate of gas (carrier gas + reagent) in each nozzle is  $1 \text{ m}^3/\text{cm}$  width of substrate / hr, at the operating temperature.

The coating process was continued until the geometrical thickness of the coating formed on the substrate was 11 nm. The substrate was then subjected to a second coating. A reagent consisting of stannic chloride, vaporised in a current of anhydrous nitrogen gas at about  $600^\circ\text{C}$ , is fed in at the first nozzle. Water vapour is conducted to the second nozzle. The water vapour is superheated to about  $600^\circ\text{C}$ , and is also injected into a carrier gas, which is air heated to about  $600^\circ\text{C}$ . The flow rate of gas (carrier gas + reagent) in each nozzle is  $1 \text{ m}^3/\text{cm}$  width of substrate/hr, at the operating temperature.

The second coating process was continued until the geometrical thickness of the tin oxide coating formed on the substrate, superimposed on the nitride coating layer, was 30 nm.

As a variation of Example 1, a silicon oxide coating layer is formed on the substrate before formation of the TiN layer. This permits to reduce interaction between  $\text{TiCl}_4$  and the substrate. The glass is coated in a coating station located at a position along the float chamber where the glass is at a temperature of about  $700^\circ\text{C}$ . The supply line is fed with nitrogen, and silane is introduced thereto with a partial pressure of 0.25%, and oxygen is introduced with a partial pressure of 0.5%. The layer formed is of silicon dioxide about 70 nm in thickness.

The glazing panel described above had an intense blue colour on reflection from the un-coated side. Various properties of the panel were measured and found to be as set out in Table III below.

EXAMPLES 2 TO 7

Using a similar process to that described in Example 1, other samples were prepared. Details of the coatings and the properties of the panels so formed were as set out in Table III below:

TABLE III

EXAMPLE:	1	2	3	4	5	6	7
Nitride	TiN	TiN	TiN	TiN	TiN	TiN	TiN
Thickness (nm)	11	15	20	25	31	40	31
Tolerance ( $\pm$ %)	15	6	12	8	10	4	4
Oxide	SnO <sub>2</sub>	SnO <sub>2</sub>	SnO <sub>2</sub>	SnO <sub>2</sub>	SnO <sub>2</sub>	SnO <sub>2</sub>	TiO <sub>2</sub> <sup>a</sup>
Thickness	30	27.5	20	17.5	10	10	10
Tolerance ( $\pm$ %)	7	3	12	9	15	16	15
T <sub>L</sub> (%)	52	45	37	31	25	19	25
<sup>1</sup> FS (%)	55	49	42	38	34	29	34
<sup>1</sup> R <sub>L</sub> (%)	15	17	17	20	21	25	21
<sup>1</sup> T <sub>L</sub> /FS	0.96	0.93	0.86	0.81	0.73	0.65	0.73
T <sub>UV</sub> (%)	39.5		24.8	19.8		9.9	
Reflected colours	<----- neutral from the coated side /blue from the un-coated side ----->						
<sup>2</sup> Purity (%)	22	22	21	19	15	8	15

a = anatase form

<sup>1</sup> = as measured from the un-coated side

5        <sup>2</sup> - "purity" means the purity of the colour as measured by reflection from the un-coated side

The tolerances quoted in the above Table III are the variations in coating thicknesses which are possible without having a perceptible effect on the properties of the finished product.

10        The above Examples 1 to 6 demonstrate that, for a substantially constant total coating thickness, changes in optical properties can be obtained by variations in the relative thicknesses of the nitride and oxide layers while the reflected colour remains substantially constant. Example 7 demonstrates the properties obtainable when the tin oxide of Examples 1 to 6 is replaced by  
15        anatase. Similar results can be obtained if the titanium nitride is replaced by zirconium nitride or niobium nitride.

#### EXAMPLE 8

20        In a further example, a solar control glazing panel having a neutral aspect is formed. The coating layers are the same as in Example 1, but the glazing panel is viewed from the coated side instead of from the un-coated side. The measured properties were:

$$T_L = 52\%$$

$$F_S = 53\%$$

$$R_L = 14\%$$

$$T_L/F_S = 0.98$$

$$T_{UV} = 39.5\%$$

5

The dominant wavelength in reflection from the coated side was 491 nm, with a purity of 3.9% (neutral aspect).

## CLAIMS

1. A pyrolytically coated glazing panel comprising a substrate, an undercoat layer comprising a nitride selected from nitrides of titanium, zirconium, niobium and mixtures of two or more thereof and an exposed transparent overcoat layer adjacent said undercoat layer comprising an oxide, characterised  
5 in that the total geometrical thickness of the undercoat and overcoat layers is between 20 nm and 55 nm.
2. A glazing panel according to claim 1, wherein the geometrical thickness of the undercoat layer is between 10 nm and 50 nm.
3. A glazing panel according to claim 1 or 2, wherein the  
10 geometrical thickness of the overcoat layer is between 9 nm and 35 nm, preferably from 15 to 35 nm.
4. A glazing panel according to any preceding claim, wherein the refractive index of the overcoat layer is from 1.8 to 2.7.
5. A glazing panel according to any preceding claim, wherein the  
15 oxide of the overcoat layer is selected from oxides of aluminium, silicon, magnesium, tin, zinc, zirconium, titanium, bismuth, niobium, and mixtures of two or more thereof.
6. A glazing panel according to any preceding claim, wherein the overcoat layer is selected to provide enhancement of the purity of colour  
20 reflected from the un-coated side of the panel.
7. A glazing panel according to claim 6, wherein the nitride of the undercoat layer comprises titanium nitride and the oxide of the overcoat layer comprises tin oxide.
8. A glazing panel according to any preceding claim, wherein the  
25 composition and thickness of the undercoat and overcoat layers are such that the dominant wavelength reflected from the un-coated side of the panel in the visible region lies within the range of 470 to 490 nm.
9. A glazing panel according to claim 8, wherein the purity of colour reflected from said un-coated side is greater than 5%.
10. A glazing panel according to any preceding claim, further  
30 comprising a further coating layer positioned between said undercoat layer and said substrate.
11. A glazing panel according to claim 10, wherein the geometrical thickness of said further layer is between 50 and 100 nm.

12. A glazing panel according to claim 10 or 11, wherein said further layer is comprised of an oxide.

13. A glazing panel according to claim 12, wherein the said further layer is comprised of silicon oxide.

5 14. A process for forming a coated glazing panel comprising the steps of:

(i) forming an undercoat layer over a substrate by pyrolysis, said undercoat layer comprising a nitride selected from nitrides of titanium, zirconium, niobium and mixtures of two or more thereof; and

10 (ii) forming an exposed transparent overcoat layer adjacent said undercoat layer by pyrolysis, said overcoat layer comprising an oxide;

characterised in that the coating of said undercoat and overcoat layers is such that the total geometrical thickness thereof is between 20 nm and 55 nm.

15

<b>Relevant Technical Fields</b>  (i) UK Cl (Ed.N) C7F (FHB, FHE, FHX) (ii) Int Cl (Ed.6) C03C 17/34; C23C (14/06, 14/08, 16/30, 16/34, 16/40, 18/12, 28/04)	Search Examiner P G BEDDOE
	Date of completion of Search 14 SEPTEMBER 1995
<b>Databases (see below)</b> (i) UK Patent Office collections of GB, EP, WO and US patent specifications.  (ii) ONLINE: WPI, CLAIMS	Documents considered relevant following a search in respect of Claims :- 1-14

Categories of documents

<b>X:</b> Document indicating lack of novelty or of inventive step.	<b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.
<b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.	<b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.
<b>A:</b> Document indicating technological background and/or state of the art.	<b>&amp;:</b> Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2262749 A (GLAVERBEL) see especially example 14	1-3, 5, 14
X, P	EP 0650938 A1 (SAINT-GOBAIN) 3 May 1995 see examples and Claims 3, 6	1, 14
X	EP 0548972 A1 (ASAHI) see especially example 13 and comparative example 6	1-3, 5
X	EP 0530676 A2 (NIPPON) see especially Table 1 samples 4, 5; Table 4 samples 3, 4, 5	1
X	WO 90/09883 A1 (LIBBEY-OWENS) see especially page 14 lines 1-12	1-3, 5, 14
X	US 5183700 (VIRATEC) see especially layers 4, 5 in table 3	1-3, 5, 14
X	WPI Accession No 91-040588/06 & JP 2307843 A (ASAHI) see abstract	1-3, 5
X	WPI Accession No 88-261499/37 & JP 63190742 A (ASAHI) see abstract	1-3, 5

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents)